

A CONTRIBUTION TO THE "CHEMISTRY OF ALUNITE."

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The total disappearance of all forms of potash for fertilising purposes from the Western Australian market during the past few years, and the insistent demands of fruit-growers and market gardeners for supplies, have led to an investigation being made of the various potash-bearing minerals of this State in the Geological Survey Laboratory of Western Australia with a view to supplying this need. Many of the results of this investigation have already been published by Dr. E. S. Simpson in an official bulletin "Sources of Industrial Potash in Western Australia."

It has been the author's privilege to more fully investigate the chemical properties of alunite—a basic sulphate of potash and alumina—a mineral which occurs in large quantities in this State and gives most promise of yielding commercial supplies of potash.

The results obtained are of sufficient importance to be set out in detail, both as supplying data as to the chemical properties of the mineral for the information of mineralogists, and as supplying information which, it is hoped, will regulate the practice of using the mineral as a source of potash for agricultural purposes.

A complete isomorphous series of minerals is known, ranging from practically pure $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ to practically pure $Na_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$. Commercially, any member of this series containing an appreciable amount of potash is known as alunite. Strictly, only those members of the series lying between the pure potash compound and the mineral containing equal molecules of potash and soda would be alunite, whilst an excess of soda molecules over potash molecules would indicate the mineral known as natro-alunite.

The most important deposits of alunite in Western Australia are situated at Kanowna and are dealt with very fully in Bulletin No. 77 of the Geological Survey of W.A. The following remarks

* By permission of the Director of the Geological Survey of Western Australia.

and results apply to experiments, etc., carried out, except when otherwise stated, on the mineral from that locality.

The Kanowna alunite is a white, firm, finely crystalline mass, resembling somewhat in appearance a compact clay, for which it might readily be mistaken. It breaks, when freshly mined, with a typical snap similar to the breaking of a biscuit. After exposure to air for a few days in a comparatively dry atmosphere many specimens of the mineral disintegrate into a fine powder, due to the presence of admixed salts. If allowed to partly dry and then again wetted, it shows a tendency to soften and crumble; this is probably due to partial dehydration and then absorption of water by the colloids (*i.e.*, clay, etc.) present. The mineral is extremely porous and tests carried out on several pieces dried at 80°C. gave 22.0, 18.1 and 10.8 per cent. of water absorbed by weight, the air space by volume being 58.3, 48.0 per cent., and 28.6 per cent., respectively.

The powder, under the microscope, appears as minute, colourless, transparent, cubical grains, which have been determined by Dr. Simpson as "not true cubes of the isometric system, but rhombohedrons approximating to cubes." This is shown by their optical properties, the crystals being anisotropic with diagonal extinction. The individual crystals are very minute, ranging in size from 3 to, at the most, 10 microns. The specific gravity was determined in methylene iodide and proved to be very close to that of quartz, *viz.*, 2.65. The refractive index was determined by mounting some of the powder on slides with liquids of known refractive index and examining them under a microscope. The mineral agreed with that of oil of cassia, having a refractive index of 1.58.

The refractive index affords a simple and ready method for the detection of alunite by immersion. The mean refractive indices of minerals resembling alunite in appearance are—

Kaolin	1.54
Quartz	1.547
Sericite	1.587
Calcite	1.601
Magnesite	1.72

The alunite from Kanowna is invariably associated with appreciable amounts of water soluble salts and a little quartz, kaolin and mica.

The empirical formula for alunite is—



which may be represented as $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$, but for reasons which will be dealt with later, would be more correctly written as $\text{K}_2\text{SO}_4 \cdot 3\text{HOAlSO}_4 \cdot 3\text{Al}(\text{OH})_3$.

Dr. Simpson suggests the following structural formula for alunite:—

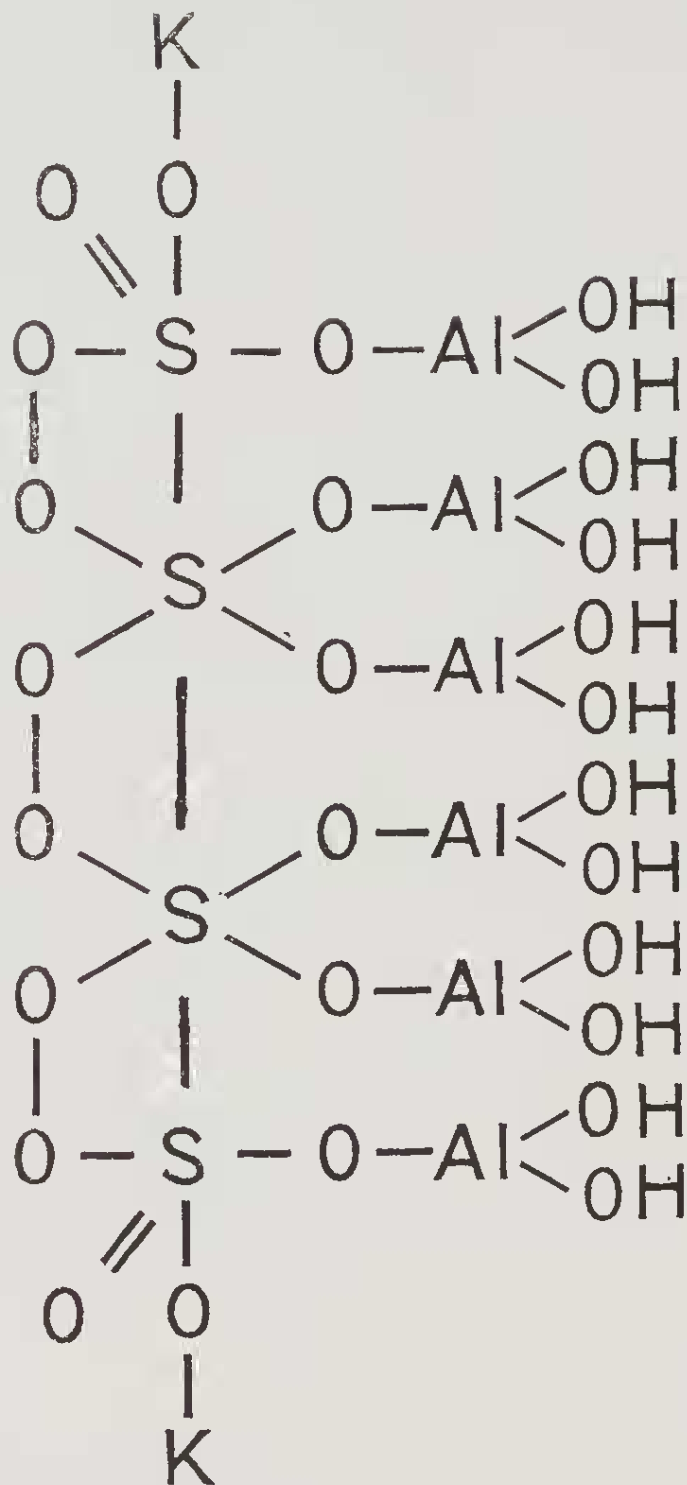


Plate IX.—Structural formula for alunite.

The composition of typical West Australian alunites is given in the accompanying table:—

ANALYSES OF ALUNITE AND NATRO-ALUNITE.								
	A.	B.	C.	D.	E.	F.	G.	H.
	Alunite, Edjudina District.	Natro-alunite, G.M.L. 2, Kalgoorlie.	Alunite, G.M.L. 1159, Kanowna.	Alunite, M.L. 12X, Kanowna.	Natro-alunite, P.A. 506, Kanowna.	Impregnated Clay, G.M.L. 918, Kanowna.	Natro-alunite Matrix, P.A. 506, Kanowna.	Natro-alunite Matrix, P.A. 506, Kanowna.
	%	%	%	%	%	%	%	%
H ₂ O+	13.23	15.19	14.55	...	15.45	2.80	2.63	6.70
K ₂ O	8.02	2.46	9.32	7.56	5.42	3.10	2.41	2.19
Na ₂ O	1.54	4.90	2.14	2.56	4.07	.40	1.00	.60
Al ₂ O ₃	33.24	36.23	35.01	...	36.46	13.08	15.17	21.96
SO ₃	35.37	36.52	37.84	37.45*	37.64	1.24	.01	.05
Fe ₂ O ₃	.61	1.24	.7924	.68	.13	.15
MgO	None	.15	None	...	None	.36	.15	.03
CaO	.24	None	None	...	None	None	None	None
SiO ₂	7.40	2.61	.4595	78.44	77.21	66.94
P ₂ O ₅	.09	.56
TiO ₂24	.20
H ₂ O—	.32	.33	None	.42	.06	.03	.10	.26
NaCl	None†	None†	None†	...	None†	None†	.79	.88
Other soluble Salts	None	None	None	...	None	None	.25‡	.25§
Density	100.06	100.19	100.10	...	100.29	100.13	100.09	100.28
Analyst
	H. Bowley.	A. J. Robertson.	H. Bowley.	H. Bowley.	E. S. Simpson.	H. Bowley.	S. Gillies.	S. Gillies.

* Includes 0.13 SO₃ soluble in water.

† Washed with water before analysis.

‡ Includes SO₃ 0.08.

§ Includes SO₃ 0.06.

EFFECT OF DRY HEAT.

The commercial utilisation of alunite in the past has been based on the formation of potash alum through the dissociation of the mineral by heat and then by wetting the roasted product. The theory of the process needs verification and, in the opinion of the author, the effect of heating alunite is not to form a true alum, but a basic sulphate of alumina and alkalis. The following experiments were carried out with a view to ascertaining the effect of dry heat at varying temperatures:—

100° Centigrade.

The sample of alunite (D) used in this experiment was crushed to pass a 30 mesh screen, the major portion passing a 90 mesh. The mineral was dried in a water oven at 98°C. to remove hygroscopic water, cooled, and then weighed: It was then reheated for one hour and again weighed, the loss being equal to 0.01 per cent. It was again placed in the water oven for two hours and the weight again taken, showing a loss of only 0.002 per cent. It is evident, therefore, that at the above temperature, the mineral is practically unaffected.

200° Centigrade.

The mineral used in the previous experiment was heated to a temperature of 200°C and weighed; it was again heated for one hour at 200°C, and again weighed. No loss at all was recorded. Alunite is, therefore, unaffected at temperatures up to 200°C.

300° Centigrade.

A sample of alunite (D) containing 0.42 per cent. of hygroscopic water was heated to a temperature of 300°C., and showed a loss of 0.49 per cent.

The mineral is, therefore, unaffected at temperatures up to 300°C.

418° Centigrade.

One gm. of a sample (D) containing 99 per cent. alunite, was heated in a gas muffle gradually to the temperature of the melting point of pure zinc (418°C.). To prevent any oxidation of the zinc indicators, the metal was enclosed in sealed combustion glass tubes. The heating was stopped as soon as the zinc melted, the charge cooled and weighed. The tests were repeated until a further loss was inappreciable.

The successive losses in per cent. noted were:—2.36 per cent., 3.06 per cent.; 5.80 per cent.; 7.48 per cent.; 8.34 per cent.; 8.95 per cent.; 9.29 per cent.; 9.42 per cent.; 9.63 per cent.; 9.67 per cent.

The total loss recorded was equivalent to $4\frac{1}{2}$ mols. of water, if it was water only, and not a mixture of H_2O and SO_2 .

In order to ascertain if any of the sulphur trioxide was volatilised, the residue was dissolved in 5 per cent. caustic soda solution, the sulphur content of which was known, and the sulphur trioxide determined. The results proved that there was no appreciable loss of SO_2 .

NaOH soluble SO_2 in raw mineral 37.09 per cent.

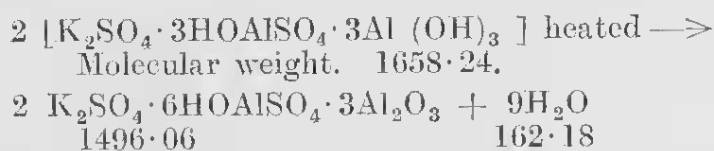
NaOH soluble SO_2 in mineral after

roasting 36.96 „

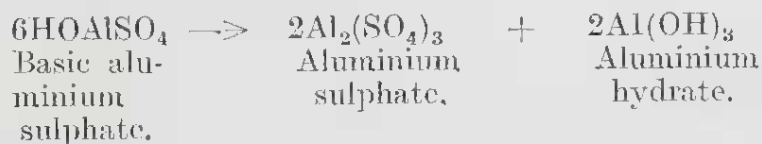
The roasted mineral was readily soluble in lukewarm 5 per cent. NaOH solution, whilst the raw mineral required several minutes on a water oven to complete solution.

The roasted mineral was only very slowly attacked by water, a portion of it dissolving and at the same time producing a voluminous precipitate of aluminium hydrates. A sample of commercial potash alum ignited at the same temperature proved to be fairly readily soluble in warm water and only produced a slight precipitate. The foregoing suggested that, on roasting alunite at the temperatures mentioned, a basic sulphate of aluminium was formed, which, on the addition of water, hydrolysed and precipitated aluminium hydrate. It was considered possible that the precipitate formed may be a basic sulphate of aluminium, but, on dissolving it in hydrochloric acid and adding barium chloride solution, only traces of sulphates were detected.

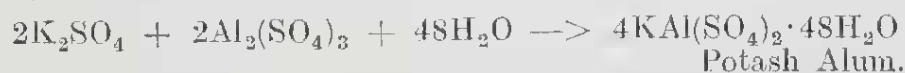
The reactions taking place at this stage may be expressed thus:—



On the addition of water to the roasted product the basic sulphate formed dissociates, precipitating aluminium hydrate, leaving aluminium sulphate in solution, thus:—



The completed equation for the formation of alum from roasted alunite is—



Alum is not formed by roasting but only by a subsequent series of reactions after the addition of water. It therefore appears that the effect of heat at the above temperature is to remove the water immediately attached to the aluminium, shown in the formula as attached to the potentially free alumina.

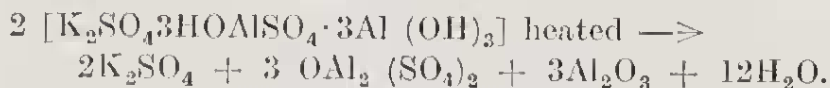
525° Centigrade.

Two separate lots of the mineral were then heated in a similar manner to a temperature of 525°C., the melting point of stibnite, a natural sulphide of antimony. The results obtained were as follow:—

Mineral	...			A.		B.
	...			2 gms.	%	1 gm.
Loss	·0762 gms.	3·81	9·11
				·0876 "	4·38	13·01
				·1632 "	8·16	13·04
				·2396 "	11·98	
				·2513 "	12·565	
				·2569 "	12·845	
				·2602 "	13·01	
				·2612 "	13·06	
				·2616 "	13·08	

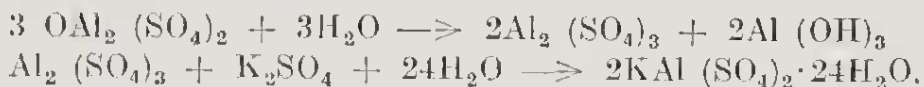
In the first series the heating was gradual, the test being withdrawn as soon as the indicator melted, weighed, and reheated to the same temperature, the process being repeated until the loss was inappreciable. The test in the second series was allowed to remain in the furnace several minutes after the melting of the stibnite.

The loss found in both cases is equal to the total water present and the residue showed practically no loss of SO_3 . The residue was partly soluble in water, forming at the same time a sticky gelatinous mass. On warming the water extract a bulky precipitate of aluminium hydrate was formed. The equations are:—



The theoretical loss to satisfy this reaction is 13.04 per cent.

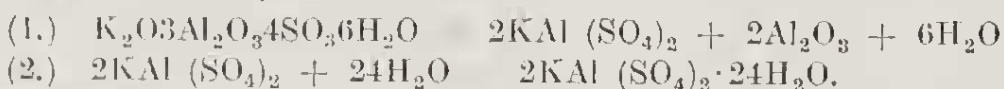
On adding water to the roasted product and warming, aluminium hydrate is precipitated and potash alum formed in solution.



The reactions proved by those experiments differ from those hitherto accepted. Thus Waggaman* states—

on heating to a moderate temperature (500° C.) water is driven off and the mineral decomposes into alumina and potassium sulphate.

He makes no mention of the formation of a basic sulphate of alumina but states, *inter alia*, that, in Italy, for the production of alum after calcining the ore at low red heat.....it is exposed in the air for several weeks or months, being moistened with water from time to time..... The reactions are represented thus:—



* U.S. Dept. Agric. Bull. 415, p. 2.

E. Sorel*, whose description of the La Tolfa method of treatment of alunite is the most detailed on record, says:—

The treatment of the alunite rock begins with a very moderate roasting, which by dehydrating the excess of the alumina, renders it insoluble. But it is necessary to be very careful not to push the temperature too far, for the sulphate of aluminium would be partially decomposed and would set free a mixture of sulphurous and sulphuric anhydrides with oxygen.

It is probable, when the proportion of sulphuric acid is greater than that which corresponds to the quantity of alum equivalent to the potash present, that there is formed, under the action of heat, an insoluble basic sulphate of aluminium, $6\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3$ †. Under the action of a temperature sufficient to liberate the vapours of sulphuric anhydride, one would obtain potassium sulphate in excess, alum, and a still more basic sulphate of aluminium, $7\text{Al}_2\text{O}_3 \cdot 5\text{SO}_3$.

From the results obtained by the writer, it appears that on heating alunite at temperatures up to 500° Centigrade, free potassium sulphate and a basic sulphate of aluminium are formed and not an anhydrous alum. This would also explain the necessity for exposing the calcined mineral to air and moisture for many weeks for the production of potash alum after calcining at the above temperatures.

801° Centigrade.

On heating the mineral to a temperature of 801° C. (melting point of common salt), the whole of the water and three-quarters of the sulphur trioxide is driven off, leaving a residue of potassium sulphate and alumina.

One gram of the mineral heated in a gas muffle at the above temperature gave the following losses:—

(1)	(2)
41.44	41.76

The equation is—



In this and previous quotations, Na_2SO_4 replaces K_2SO_4 to an extent proportional to the Na which substitutes K in the original mineral.

The theoretical loss to satisfy this equation is 42.0 per cent.

The potassium sulphate formed is readily dissolved in water and the solution shows no tendency to produce a precipitate on warming. With a view to determining the conditions under which the whole of the potassium sulphate could be leached out of the calcined mass, several lots of the alunite ore were calcined under similar conditions and leached with water for varying lengths of time,

* La Grande Industrie Chimique Minérale, p. 716.

† 2 is probably a misprint in the original for 5.

the potash and soda being determined in the filtered extract. The results obtained were:—

(a) Half-gram of mineral, roasted, moistened with 50 cc. cold water and let stand overnight; the solution was decanted off, then 50 cc. of hot water added, warmed for one hour on water bath, filtered and washed with hot water.

(b) Half-gram of mineral, roasted, taken up with 50 cc. hot water, allowed to stand on water bath for one hour with frequent stirring, decanted and retreated for a further hour with 50 cc. water, filtered and washed with boiling water.

(c) Half-gram of mineral, roasted, taken up with 100 cc. hot water and allowed to stand on water bath for 5 hours with occasional stirring, then decanted and treated for a further 3 hours in a similar manner, then filtered and washed.

(d) Half-gram of mineral, roasted, taken up with 50 cc. of water, allowed to stand for one hour on a water bath with frequent stirring, then filtered and washed with boiling water. The residue was then transferred to the beaker and retreated for a further hour under similar conditions, again filtered and washed and then again retreated.

							Potash.	Soda.
							%	%
(a.)	4.98	2.92
(b.)	4.96	2.94
(c.)	5.00	2.90
(d.)	First extract	4.66	2.76
	Second extract36	.18
	Third extract	traces	traces
							5.02	2.94

These figures show that after calcining the mineral at 800° C. the potassium sulphate formed is very readily soluble in warm water.

Another sample (D) of high grade alunite, giving an ignition loss of 41.44 per cent. gave the following figures:—

							2 hours leach- ing.	3 hours leach- ing.
							100 cc. water	100 cc. water.
							%	%
NaCl + KCl	16.18	16.20
K ₂ O	7.10	7.10
Na ₂ O	2.54	2.55

960° Centigrade.—To determine the effect of over roasting in the presence of common impurities, one half-gramme lot of a low grade alunite ore was heated to the melting point of silver (960° C.) and the results showed a loss of water soluble potash due to the formation of an insoluble potassium compound, probably a potassium alumino-silicate, by interaction between the first formed

potassium sulphate and the associated silica and silicates. The results obtained were:—

	Calcined at 801° C.	Calcined at 960° C.
	%	%
Ignition loss	29·08	30·54
Water soluble Potash, K_2O	4·02	3·70
Water soluble Soda, Na_2O	2·49	2·22

The increased ignition loss in this case is due to the dissociation of the potassium and sodium sulphates.

SOLUBILITY OF ALUNITE.

The production of water soluble potash from alunite for fertilising purposes by roasting has proved to be a fairly costly process, entailing the employment of an extensive roasting plant. The fuel consumption has been found to be excessive owing to the fact that the reactions taking place are endothermic; and the necessity of keeping the temperature within comparatively narrow limits is a severe tax on the staff.

Owing to the fact that very little information was obtainable showing the solubility of the mineral in various reagents, the following experiments were carried out with a view to ascertaining if some cheaper method could be evolved for rendering the potash available as a plant food.

SOLUBILITY IN WATER.

The only direct references to the effect of water upon alunite which could be found were those of Waggaman and Cullen* and of James,† who both say that alunite is "insoluble in water."

In view, however, of the rapid solution of alunite by caustic alkali solution, it appeared probable that its solubility in pure water was appreciable.

The material chosen for this test was soft and porous. It was over 99 per cent. pure, containing K_2O , 7.56 per cent; Na_2O , 2.56 per cent.; the impurities being quartz with traces of kaolin, muscovite, limonite, epsomite and common salt.

This material was crushed to pass a 30-mesh sieve, the major part passing also a 90-mesh sieve. One gramme was placed in a silica beaker, covered with 100 cc. water and stirred at frequent intervals with a platinum rod. At the end of one day the solution was decanted through a small dense filter and the filtrate evaporated to dryness in a weighed platinum dish, dried at 200° C. and weighed. Thereafter the process was repeated four times, the length of standing being increased to two days, but the same gramme of ore and the same filter was used throughout. The temperature ranged from 15° C. to 25° C., an average of 20° C. Owing to the tendency of much of the finest alunite to float on the surface of the water, there should be no doubt as to the saturation of the

* U.S. Dept., Agric. Bull. 415, p. 2.

† Comm. of Aust., Adv. Counc. of Sci. and Ind., Bull. No. 3, p. 9.

solution under these conditions. The weight of the extractions was corrected by a blank on the distilled water used. Owing to the fact that this contained a little organic matter the final weighings were made after heating to a temperature of about 400° C., which was sufficient to drive off this organic matter and dehydrate the alunite taken into solution. The first extract (0.0048 gm.) contained the greater part of the associated epsomite and salt. The second extract contained a little, and the third probably traces, but the fourth and fifth should not have been contaminated. The solubilities shown by these two were, in 100 cc.

4th 0.0003 grammes.

5th 0.00025 „

The mean solubility, therefore, of alunite in 100 cc. of pure water at 20° C. is 0.00027 grammes.

This is of the same order as that of barite (BaSO_4), which is 0.00023 grammes.

SOLUBILITY IN CAUSTIC ALKALIS.

No mention is made by Dana and Leeroix, two well recognised authorities on mineralogy, of the effect of solutions of KOH and NaOH upon alunite. Janes* says "It is readily soluble in caustic alkalis."

The material used in these experiments was 99 per cent pure, containing 7.56 per cent. K_2O and 2.56 Na_2O , the impurities being a little quartz, kaolin, and water soluble sulphates.

One half gramme lots of the mineral were treated with different strengths of NaOH solution for varying lengths of time and at different temperatures, being stirred well from time to time. The solutions were then filtered and washed well with hot water; the filtrates were just acidified with hydrochloric acid, boiled to expel any CO_2 present, then sufficient barium chloride added and the solutions allowed to stand for a few hours. The barium sulphate was filtered off and weighed and calculated as SO_3 .

The SO_3 was determined in a blank on the reagents used and the SO_3 found plus the water soluble sulphates present in the mineral deducted from the total. The SO_3 dissolved was then calculated as alunite from a factor found by determining the total insoluble SO_3 in the sample. The figures obtained were as follow:—

1 per cent. NaOH Solution.

Alunite taken.	Sodium in Solution.	Solution. cc.	Temperature.	Time.	Alunite dissolved.
0.5gm.	0.2875	50	20° C.	2 hrs.	19.2
0.5gm.	0.2875	50	20° C.	4 hrs.	30.4
0.5gm.	0.2875	50	91° C.	2 hrs.	98.6

5 per cent. NaOH Solution.

0.5gm.	1.4375	50	20° C.	2 hrs.	84.3
0.5gm.	1.4375	50	91° C.	20 mins.	100.0

* Comm. of Aust., Adv. Coune. of Sci. and Inl., Bull. No. 3.

The equation for this reaction is:—



The whole of the products of this reaction are water soluble. The results show that alunite is readily dissolved by warm dilute solutions of caustic alkalis, a process which provides a most satisfactory method for getting the mineral into solution.

The effective agent in this reaction is the high concentration of hydroxyl ion which produces aluminate ion at the expense of the basic aluminium salt.

A. J. Robertson's experiments on Kalgoorlie natroalunite, made in the Geological Survey Laboratory in 1915, showed that this mineral passed wholly into solution on warming for 20 minutes with 5 per cent. KOH solution.

SOLUBILITY IN SODIUM CARBONATE.

No references were obtained showing the effect of sodium carbonate solutions on alunite. Knowing that caustic alkalis exert a very rapid solvent effect, and that sodium carbonate hydrolyses freely in water, experiments were carried out with a view to determining the solubility of alunite in sodium carbonate.

The solution used in these experiments contained the same amount of sodium as that in the case of the caustic soda tests. The temperature and time of experiment were also the same, so that the results as to rate of solubility would be comparable. The material also was that used in the caustic soda tests and was treated in exactly similar manner.

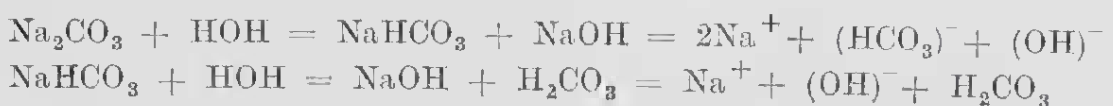
1.325 per cent. Na_2CO_3 Solution.

Alunite.	Sodium in Solution.	Solution, cc.	Temperature.	Time.	Alunite dissolved.
0.5gm.	0.2875	50	20° C.	2 hrs.	0.13
0.5gm.	0.2875	50	20° C.	4 hrs.	0.35
0.5gm.	0.2875	50	91° C.	2 hrs.	43.85

6.625 per cent. Na_2CO_3 Solution.

0.5gm.	1.4375	50	20° C.	2 hrs.	1.09
0.5gm.	1.4375	50	91° C.	2 hrs.	71.60

It will be noted that Na_2CO_3 has very little effect on alunite in the cold, but the attack is considerably increased in warm solutions. From this it is apparent the solubility is due to the hydroxyl ions present, the Na_2CO_3 hydrolysing to form NaOH and H_2CO_3 . The reaction may be expressed thus:



SOLUBILITY IN CAUSTIC LIME SOLUTIONS.

In view of the rapid and complete solution of alunite in caustic alkalis, and to obtain a cheaper and more readily available solvent, the effect of caustic lime solutions, which also contain a considerable concentration of hydroxyl ion, were tried on the mineral.

The material used for the preliminary tests was 99 per cent. pure, containing K_2O , 7.56 per cent.; Na_2O , 2.56 per cent. The impurities were mainly quartz and kaolin with small amounts of epsomite and salt.

Several grammic lots of the mineral were placed in quartz beakers with 100 cc. of water and 0.25 gm. of freshly burnt lime. The solutions were stirred occasionally and allowed to stand in the cold for periods of one, two, and eight days. The solutions were then filtered and the potash and soda estimated in the extract. It was noticed after one day that a bulky gelatinous precipitate was formed, quite distinct in appearance from the original alunite. This proved on examination to be calcium aluminatc. The results obtained were—

	Potash,	Soda.
	%	%
Originally in Sample	7.56	2.56
In solution after one day's treatment	0.71	1.15
In solution after two days' treatment	1.09	1.26
In solution after eight days' treatment	1.16	1.45

These figures were considered so satisfactory that arrangements were made to carry out a systematic series of experiments, the results of which are shown below.

These tests were carried out on three separate lots of the mineral containing the following amounts of—

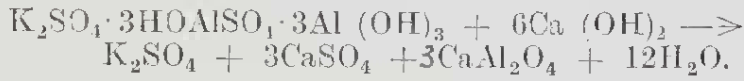
	1	2	3
Alunite	95.05	96.55	97.31
Total Potash	6.46	8.54	7.98
Total Soda	3.62	2.24	2.60

The samples were crushed to pass a 30-mesh sieve, the greater portion of which would pass a 90-mesh sieve. One half gramme of the mineral was placed in a resistance flask with 400 cc. of a freshly prepared solution containing the amount of calcium hydrate shown in the table. (The solubility of $Ca(OH)_2$ in water is 1.7 gms. per litre.) Several pieces of glass rod were placed in the flask which was then tightly stoppered with a waxed cork and the tests shaken vigorously from time to time. At the expiration of the time allowed the precipitate was filtered off, well washed with hot water, and the potash and soda which had passed into solution estimated by the platonic-chloride method.

It was noticed that in the case of treatment with caustic alkalis the alunite goes completely into solution, but with caustic lime a bulky precipitate was formed. This precipitate was examined after

washing well to remove all the calcium sulphate, and found to consist of calcium aluminate and undecomposed alunite.

The results shown in Table I, were obtained by treating the 0.5 gm. of the mineral with 0.5308 gms. of caustic lime, which is considerably more than necessary to satisfy the following equation, the theoretical quantity being 0.2029 gms. of CaO or 0.2679 Ca(OH)₂.



Sample No.	Lease and Grade of Alumite.	Ore taken.	Solution used.	Ca(OH) ₂ in Solution.	Time of Digestion.	Dissolved Alkalies		Dissolved % of Total Potash.	Dissolved % of Extractable Potash.
						K ₂ O.	Na ₂ O.		
5811E	McKinley & party, "Shamrock," M.L. 12 ⁶ 95.05 %	gms. 0.50	cc. 400	% 0.1327	Days. 1	% 2.97	% 2.03	46.0	47.2
"	"	"	"	"	2	3.87	3.41	59.0	61.5
"	"	"	"	"	3	5.21 (3.09)	(3.09)	80.6	82.8
"	"	"	"	"	4	5.51	3.44	85.3	87.6
"	"	"	"	"	7	5.77 (3.03)	(3.03)	89.3	91.7
"	"	"	"	"	" Extractable "	6.29	3.41	97.4	...
"	"	"	"	"	Total	6.46	3.62	100.0	...
5824E	Emde & Curran's "Breakaway," 96.55%	gms. 0.50	cc. 400	% 0.1327	Days. 1	2.47	1.18	28.0	29.1
"	"	"	"	"	2	3.97	1.70	46.5	46.8
"	"	"	"	"	3	5.33	2.20	64.7	62.5
"	"	"	"	"	4	6.29	2.23	73.8	74.3
"	"	"	"	"	7	6.87	2.24	80.5	81.0
"	"	"	"	"	" Extractable "	8.48	2.07	99.3	...
"	"	"	"	"	Total	8.54	2.24	100.0	...
5825E	Fletcher & party, P.A. 518, 97.31 %	gms. 0.50	cc. 400	% 0.1327	Days. 1	2.46	1.46	30.8	31.3
"	"	"	"	"	2	5.57	1.84	68.5	69.5
"	"	"	"	"	3	6.59	2.24	82.6	83.7
"	"	"	"	"	4	6.93	2.38	86.8	88.1
"	"	"	"	"	7	7.10	2.46	89.0	90.2
"	"	"	"	"	" Extractable "	7.87	2.56	98.6	...
"	"	"	"	"	Total	7.98	2.60	100.0	...

* Soluble in water after calcining the mineral at 800° C.

The above figures proved that almost saturated but still weak (one-fiftieth normal) solution of Ca(OH)₂ under suitable conditions, completely decomposes alunite, all the potash going into solution.

KANOWNA ALUNITE.

DIGESTION EXPERIMENTS WITH LIME.

SERIES II., TEMPERATURE ATMOSPHERIC.

Sample No.	Lease and Grade of Alunite.	Ore taken.	Solution used.	Ca(OH) ₂ in Solution.	Time of Digestion.	Dissolved Alkalies.		Dissolved per cent. of Total Potash.	Dissolved per cent. of "Extractable" Potash.
						K ₂ O.	Na ₂ O.		
5811E	McKinley & Party, "Shamrock," 95.05 %	gms. 0.45	cc. 400	% .0714	Days. 1	% 2.24	% 2.05	34.7	35.6
"	"	"	"	"	2	2.67	2.57	41.3	42.4
"	"	"	"	"	3	2.85	2.63	44.1	45.3
"	"	"	"	"	4	3.38	2.64	52.3	53.7
"	"	"	"	"	7	3.36	2.27	52.0	53.4
"	"	0.50	" Extractable"*	6.29	3.41	97.4	...
5824E	Emde & Curran's, "Breakaway," 96.55 %	gms. 0.45	cc. 400	% .0714	Total 1	6.46	3.62	100.0	38.7
"	"	"	"	"	2	3.86	2.00	45.2	45.5
"	"	"	"	"	3	4.01	2.11	47.0	47.3
"	"	"	"	"	4	4.52	1.73	52.9	53.3
"	"	"	"	"	7	4.88	2.04	57.1	57.5
"	"	0.50	" Extractable"*	8.48	2.07	99.3	...
5825E	Fletcher & Party; P.A. 518, 97.31 %	gms. 0.45	cc. 400	% .0714	Total 1	8.54	2.24	100.0	34.0
"	"	"	"	"	2	2.67	1.56	33.5	...
"	"	"	"	"	3	3.41	1.78	42.7	43.2
"	"	"	"	"	3	2.77	2.44	47.2	47.9
"	"	"	"	"	4	4.17	2.45	52.3	53.0
"	"	"	"	"	7	4.28	1.65	53.6	54.4
"	"	0.50	" Extractable"*	7.87	2.56	98.6	...
"	"	"	"	"	Total 1	7.98	2.60	100.0	...

5825E Special—83 gms. ore mixed into a thick paste with 38 gms. 90% lime, allowed to stand 32 days, diluted and filtered; filtrate contained 30.9% of total Potash. * Soluble in water after calcining the mineral at 800° C.

It is highly probable that if facilities be available for the removal of the end products of the reaction as they are formed, the solubility of the mineral would be considerably increased.

In order to ascertain the solubility of alunite in lime with minimum amount of water, an experiment was carried out on 1lb. (453 grams) of alunite containing K_2O , 7.84 per cent.; Na_2O , 2.72 per cent., crushed to pass a 10-mesh screen, mixed with $\frac{1}{2}$ lb. (226 grams) lime (CaO) and one gallon of water. It was allowed to stand for two days with occasional stirring and then filtered, the solution being evaporated to small bulk to remove the calcium sulphate, again filtered and evaporated to dryness. The yield of crude potassium and sodium sulphates was 0.1205lbs. (54.6 grams), equal to 70.1 per cent. of the potash and soda present in the ore.

These results are of the greatest value in the utilisation of alunite as they indicate a cheap and ready method for converting the potash of the mineral into a readily available form, and I commend them to the serious consideration of agricultural chemists.

SOLUBILITY IN CALCIUM CARBONATE SOLUTION.

No record could be found of the effect of calcium carbonate on alunite. Owing to the highly satisfactory results obtained by the treatment with caustic lime solutions and also to the fact of the general use of carbonate of lime in agriculture, it was considered advisable to carry out a systematic series of tests with solutions containing calcium carbonate. The solubility of calcium carbonate in water is very low, but calcium carbonate in solution hydrolyses, forming calcium hydrate and calcium bicarbonate, both of which have a greater solubility in water than normal calcium carbonate, but are included in the solubility, viz., 0.013 grams per litre, of $CaCO_3$ in water.

The mineral in each case was placed in flasks with 400 cc. of water and 0.716 gms. of pure precipitated calcium carbonate added; the flasks were stoppered with waxed corks and kept closed during

the whole time of the extraction. The tests were shaken vigorously from time to time. The results obtained are shown in Table III.

KANOWNA ALUNITE ORE
DIGESTION EXPERIMENTS WITH CALCIUM CARBONATE
SERIES III. TEMPERATURE, ATMOSPHERIC.

Sample No.	Lease and Grade.	Amounts used.			Time of Digestion.	Dissolved Alkalies.		Dissolved % of Total Potash.	Dissolved % of "Extractable Potash."
		Ore.	CaCO ₃ .	Distilled Water.		K ₂ O.	Na ₂ O.		
6153E (5811)	McKinley and Party, Shamrock M.L. 12, 95.65 per cent.	gms. 0.50	gms. 0.716	cc. 400	Days. 1	% 0.34	% 0.42	5.3	5.4
	"	"	"	"	2	0.44	0.42	6.8	7.0
	"	"	"	"	3	0.30	0.40	4.6	4.8
	"	"	"	"	4	0.44	0.48	6.8	7.0
	"	"	"	"	7	0.46	0.54	7.1	7.3
	"	"	"	"	"	6.29	3.41	97.4	...
6154E (5824)	Emde & Curran's "Breakaway" 96.55 per cent.	" 0.50	" 0.716	" 400	Total 1	6.46 0.30	3.62 0.34	100.0 3.5	3.5
	"	"	"	"	2	0.32	0.54	3.7	3.8
	"	"	"	"	3	0.34	0.62	4.0	4.0
	"	"	"	"	4	0.48	0.68	5.6	5.7
	"	"	"	"	7	0.60	0.76	7.0	7.1
	"	"	"	"	8.48	2.07	99.3	...	
6155E (5825)	Fletcher and Party, P.A. 518 97.31 per cent.	" 0.50	" 0.716	" 400	Total 1	8.54 0.20	2.24 0.38	100.0 2.5	2.5
	"	"	"	"	2	0.30	0.40	3.8	3.8
	"	"	"	"	3	0.40	0.46	5.0	5.1
	"	"	"	"	4	0.42	0.40	5.3	5.3
	"	"	"	"	7	0.44	0.46	5.5	5.6
	"	"	"	"	7.87	2.56	98.6	...	
"	"	"	"	Total	7.98	2.60	100.0	...	

* Soluble in water after calcining the mineral at 800° C.

The results are highly satisfactory in that they show that the alunite is attacked by solutions containing calcium carbonate, potassium sulphate going into solution. The action is considerably slower than that of caustic lime solutions, but there is little doubt that in time the effect would be the same as that of calcium hydrate

solutions. It is considered that had facilities been given for the removal of the free carbonic acid formed in these experiments, the reaction would have been considerably accelerated as the hydrolysis of the calcium carbonate would have been increased.

SOLUBILITY IN HYDROCHLORIC ACID.

Very few authorities give any information regarding the effect of hydrochloric acid upon alunite.

Rammelsberg*, however, referring to true alunite, says: "Is dissolved with difficulty by hydrochloric acid." Janes†, on the contrary, says: "Alunite is insoluble in hydrochloric acid."

As long ago as 1914 Mr. A. J. Robertson proved in the Geological Survey Laboratory that the natroalunite from the Maritana Lease at Kalgoorlie was quite appreciably attacked by warm hydrochloric acid, and that in fact, it was attacked approximately with the same rapidity as crystalline haematite. The results obtained by him on Sample "B," quoted previously, containing 36.52 per cent. of SO_3 with 4.90 per cent. of Na_2O and 2.46 per cent. of K_2O , are as follows:—

Sulphur trioxide passed into Solution.	Method of Solution.	Time.	Nature of insoluble Residue.
		min.	
1.35	Warmed with 5E HCl	10-15	White.
3.52	Warmed with 10E HCl	10	White.
6.52	Warmed with 10E HCl	20	White.
20.38	Boiled with 10E HCl	30	White.
36.52	Warmed with 5% KOH	30	Brown coloured residue and silica.

Later experiments carried out on Kanowna alunite samples, containing 37.32 per cent. of sulphur trioxide gave the following figures:—

Sulphur trioxide passed into Solution.	Temperature.	Time.	Strength of HCl.
%		min.	
0.33	70-75° C.	10	5E
0.11	75° C.	10	10E
0.49	75° C.	20	10E
4.56	100° C.	30	10E

* Rammelsberg, C. F.—Handbuch der Mineralchemie, 1875, p. 274.

† Janes, F. W.—The Alunite Deposits of Australia and their utilisation, 1917, p. 9.

SOLUBILITY IN HYDROFLUORIC ACID.

No reference could be found to the effect of hydrofluoric acid on alunite.

Owing to the close resemblance in many respects of alunite to kaolin, for which it may be mistaken, the effect of that reagent was tried to determine if this acid could be used to distinguish between the two minerals.

The mineral used for these experiments was the same as used for the solubility in caustic soda solutions, being 99 per cent. pure.

The experiments were carried out in platinum vessels and stirred from time to time. 0.5 gm. lots of the mineral were taken and the acid used in each case was equal to 5 cc., 25E hydrofluoric acid, the results being:—

Strength of Acid.	Time.	Temperature.	Alunite in Solution.
	min.		
5E	15	90° C.	Complete.
10E	30	20° C.	Little.
10E	5	90° C.	Complete.

The solution of the mineral in warm hydrofluoric acid is therefore very rapid. The solution contains a mixture of potash alum and aluminium fluoride.

SOLUBILITY IN SULPHURIC ACID.

Only one reference was found regarding the effect of sulphuric acid on alunite. James, in referring to the effect of acids on alunite, says: "Is soluble in strong sulphuric acid on heating."

The mineral on which these experiments were carried out was 99 per cent. pure, with 2.46 per cent. K_2O and 4.90 per cent. Na_2O . The results obtained were as follow:—

Strength of Acid.	Time.	Temperature.	Alunite in Solution.
5E	1 hr.	90° C.	Trace.
10E	1 hr.	90° C.	Little.
36E	1 hr.	90° C.	Much.
36E*	10 min.	200° C.	Complete.

* It was found that on cooling the solution anhydrous sulphates were thrown out of solution.

CONCLUSIONS.

(1.) Alunite is unaffected by dry heat at temperatures up to 300° C.

(2.) The decomposition of the mineral in alum roasting is in two stages. At 400° C. the mineral loses four and a half molecules of water with the formation of a basic sulphate of aluminium and potash, and on further heating to a temperature of 500° C., the remaining water is removed, forming an anhydrous basic sulphate. On the addition of water the basic sulphates dissociate, producing a true alum and precipitating aluminium hydrate.

(3.) Alunite heated to a temperature of 800° C. dissociates completely into potassium sulphate, alumina, sulphur trioxide and water. Part of the sulphur trioxide dissociates further into a mixture of sulphur dioxide and oxygen.

(4.) On heating alunite to a temperature of 960° C., the potassium sulphate formed is dissociated and interacts with the alumina to form soluble potassium aluminate, or, in the presence of silica, insoluble potassium aluminosilicates.

(5.) Alunite is readily soluble in warm dilute solutions of caustic alkali, hydrofluoric acid, and hot strong sulphuric acid.

(6.) Alunite is slowly soluble in cold solutions of sodium carbonate, but readily soluble in warm solutions of that reagent.

(7.) Alunite is moderately soluble in hydrochloric acid and warm dilute sulphuric acid.

(8.) Alunite is sparingly soluble in water.

(9.) Alunite is attacked fairly readily by a solution of caustic lime, the whole of the potash passing into solution.

(10.) Alunite is appreciably attacked by calcium carbonate solutions.

I wish to express my deep appreciation to my Chief, Dr. E. S. Simpson, who has given me every encouragement to pursue these investigations, for the great interest he has taken in this work, and the way in which he has at all times been ready to assist me with suggestions and give advice when it was most urgently needed. I wish to thank Mr. E. M. Joll for his careful work and interest shown in carrying out the digestion experiments with caustic lime and calcium carbonate. I also wish to acknowledge the courtesy of the Hon. the Minister for Mines in giving permission to publish the figures shown in Tables I., II., and III.

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